# Photo-electron spectroscopy. General theoretical aspects and the calculation of peak positions and intensities in some simple systems.

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SUMMARY

In this thesis a quantum mechanical description of photo-electron spectorscopy is presented. In addition intensities and positions of photo-electron peaks are calculated for some simple systems. The calculations are carried out with a non-orthogonal configuration interaction method (NOCI) that has not been applied before.

In chapter II a formal time-independent quantum mechanical treatment is presented of the final states that can occur on interaction with electro-magnetic radiation. At relative low photon-energies at most one electron per atom (molecule) will be emitted and the possible ion states are discrete eigenstates. All final states are coupled, however, which is important for an understanding of resonances that can occur in the cross sections such as auto-ionization.
At higher photon energies more electrons can be emitted per molecule. The observed peaks in the photo-electron spectrum can (formally) only be explained through a theory of resonant scattering. In the theory presented several kinds of resonances can be distinguished. Isolated resonances can give rise to a Lorentz-distribution in the kinetic energy spectrum of the emitted electrons. The theory indicates that at these relative high photon-energies the spectrum contains a noise-like background, which is determined by the non-resonant part of the proces. This background can be analized experimentally by coincidence measurements. The influence of the nuclear motion in molecules is briefly discussed.

In chapter III models for the calculation of absolute and relative intensities are discussed. A new derivation shows that under certain conditions the probability amplitude of a photo-electron transition is given by the product of an "effective" one-electron dipole matrix element and a "reduced" overlap-matrix element. This result is not limited to ionizations from closed shell systems or deep-lying shells. It includes the

usual intensity models for the calculation of the relative intensities of satellites as well as of the multiplet peaks in open shell systems. For closed shell systems the relative intensities of satellites can be *calculated* with this model only if the corresponding ion states have the same symmetry (monopole "selection rules"). One may not conclude that, conversily, ion states of different symmetry cannot appear as satellites of one and the same main peak (dipole "shake-up").

In chapter IV it is explained why the calculations in the subsequent chapters are carried out with an unusual method, the non-orthogonal configuration interaction method (NOCI). In the usual methods orthogonal one-electron states are employed of which only a part, the set of occupied orbitals, is optimized for the many-electron state under consideration. This leads generally to long, poorly converging, expansions for the many-electron wavefunctions to be determined. Also the results are often biased towards a particular state, usually the ground-state. For spectroscopic applications this can be a disadvantage especially if wavefunctions and energy eigenvalues are needed for a number of states of the same symmetry. The NOCI method tries to remedy this situation by first carrying out independent S.C.F. (H.F. or MCSCF) calculations for a number of states. The matrix representation of the N-electron hamiltonian in terms of the wavefunctions so obtained is diagonalized, taking the non-orthogonality of the functions into account. Essential for the method is the ability to calculate efficiently matrix elements between states described with different, mutually non-orthogonal, sets of one-electron functions. The method applied is also applicable to molecular problems, some of which are indicated. Technical details are discussed in Appendix D.

In chapters V and VI finally a number of photo-electron peaks and their relative intensities are calculated for Ne and Ar using the NOCI method and the theory of chapter III. Comparison is made with experimental data and other recent calculations. For

Ne the agreement with experiment is generally good. For Ar, where the calculations are more limited in character, the agreement is less satisfactory. It can be concluded that it is worthwhile to further explore the NOCI methode as to its applicability, especially also to electronic states of molecules.